Synergistic improvement of thermal transport properties for thermoplastic composites containing mixed alumina and graphene fillers

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ABSTRACT: In this work, a novel approach was developed for obtaining a strong three-dimensional network of heat conducting path by filling alumina (Al_2O_3) and graphene sheets (GR) into poly(ethylene-co-vinyl acetate) (EVA). This unique structure effectively prevents the inter-sheet restacking of graphene sheets and minimizes the thermal contact resistance between fillers and interface. The resultant exhibits a high thermal conductivity of 2.40 ± 0.07 W/m K, which is much higher than single filler at the same loading. Additionally, a strong synergistic effect can also be observed, and three-dimensional schematic models were simulated for this enhancement. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43242.

INTRODUCTION

Modern electronics need more efficient heat dissipation systems due to their increasing power densities and decreasing size and weight.[1–3] Thermal interface materials, applied between heat sources and heat sinks, are essential ingredients of efficient heat removal.[4–6] Thermal interface materials are usually composites: matrix filled by thermally conductive particles such as aluminum nitride, alumina and boron nitride to achieve high thermal conductivity at room temperature.[7–9] Al_2O_3 is used as a commonly filler for heat dissipation because of its excellent thermally conductive and low cost. However, high thermal conductivity of the composite usually requires high fractions of filler, which is unfavorable for processing and application. Recently, some efforts were invested to reduce the content of filler and improve the thermal properties of composites by using high thermal conductive fillers, and the typical fillers include 1D carbon nanotubes and 2D graphene sheets.[4,10–16]

Graphene, a one-atom-thick material, is a more promising filler than carbon nanotubes owing to its extreme intrinsic thermal conductivity ($\sim$5300 W/mK) through phononic transport.[17–19] In fact, great efforts have been demonstrated that embed low content of GR into epoxy matrix and greases is an effective way to improve their thermal conductivity.[20,21] Various polymer-nanocarbon based nanocomposites have been synthesized with

enhanced properties through novel strategies.[22–24] However, the thermal conductivity of these composites is still insufficient for practical applications, mainly due to the poor dispersion and restacking of GR, and weak thermal coupling at GR/base interface. Even though surfactant-assisted and non-covalent functional GR can be disperse in diverse matrix without degrading the physical and chemical properties, it is difficult to prepare high loading of graphene sheets which may cause the increased viscosity of polymer matrix because of its large specific surface.[25–27] Considering these critical issues, construct a three-dimensional thermally conductive network to decrease phonon scattering and interfacial thermal resistance is a key challenge to enhance the thermal conductivity of thermal interface materials. One possible route is to combine two fillers, which fully exploits the advantages of each filler. For example, the hybrid systems of boron nitride and multi-walled carbon nanotube (1.74 W/m K), GR and Al_2O_3 (3.45 W/m K), GR and carbon nanotube have been proved to improve their thermal conductivity.[28–30] Nevertheless, the introduction of hybrid fillers into the EVA to prepare novel thermal interface materials with high thermal conductivity has not yet been fully reported.

In this study, we suggest a simple method for obtaining high thermal conductivity of thermoplastic composites by filling with Al_2O_3 particles, GR and Al_2O_3/GR in EVA. And a strong three-dimensional network of heat conducting path was constructed
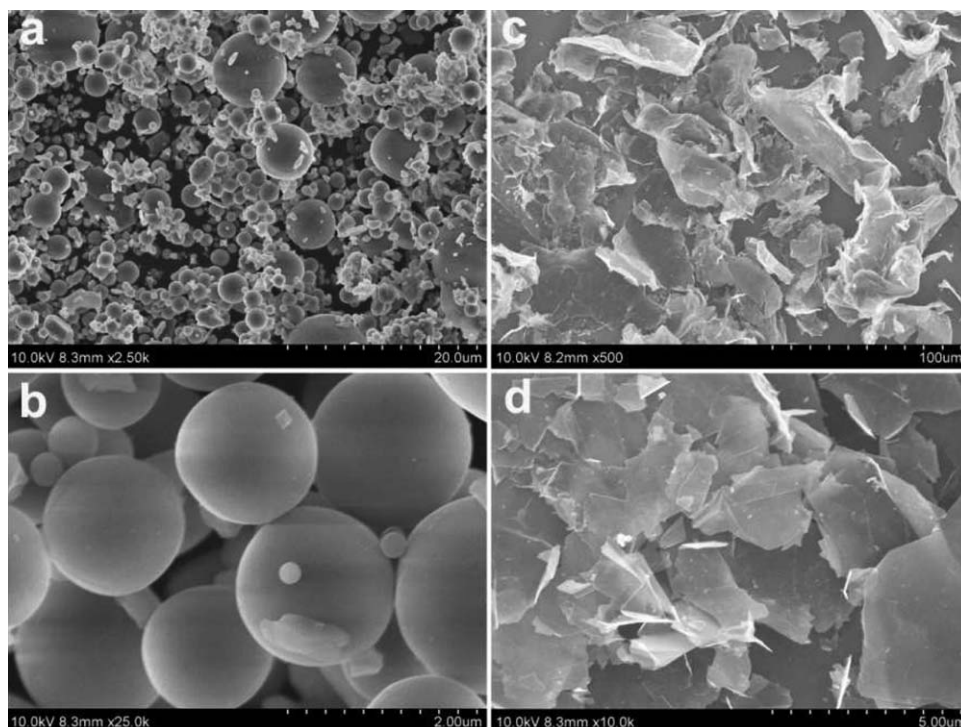
Figure 1. SEM images of Al_2O_3 particles (a,b) and GR (c,d).

when filled with Al_2O_3/GR. This unique structure effectively prevents the inter-sheet restacking of GR and minimizes the thermal contact resistance between fillers and interface. The resultant exhibits a high thermal conductivity of 2.40 ± 0.07 W/m K which is much higher than single filler at the same loading. Additionally, a strong synergistic effect can also be observed and suitable models were introduced for this enhancement. Our processes provide a new approach to prepare hybrid fillers based EVA with enhanced thermal conductivity, and new opportunities for their applications in heat dissipation.

EXPERIMENTAL

Preparation of Composites

The Al_2O_3 with a purity of 99.5% and average particle sizes of 1.4 μm were purchased from Nippon Steel Materials Co., Japan. EVA (V3430) with vinyl acetate content of 18%, a melt flow index of 1.7 g/10min (190°C, 2.160 kg) and a density of 0.94 g/cm^3 was supplied by Sinopharm Chemical Reagent Co. The graphite oxide was synthesized using the improved Hummers' method and then GR was prepared by the exfoliation of graphite oxide through thermal shock on rapid exposure to temperatures of 800°C in nitrogen for 30s.[31,32] The novel composites were prepared as follows: the Al_2O_3 different content were mixed in the right amount of EVA by using a torque rheometer at a speed of 60 rpm for 20 min, then quantitative GR was added to the mixture and dispersed at a speed of 60 rpm for another 20 min. Finally, the mixtures were transferred to a thermocompressor at 120°C under a pressure of 20 MPa and cooling to 80°C to obtain the composites. For comparison, the composites only filled with alumina particles and GR were prepared by the same procedure.

Characterization

The morphologies of Al_2O_3 and GR were determined by a field-emission scanning electron microscope (S4800, Hitachi, Japan). The phase composition and crystallinity of the Al_2O_3, GR and composites were characterized by powder X-ray diffraction (XRD) on a Bruker Advanced. The thermal conductivity of samples was measured with a thermal conductivity analyzer (C-Therm TCi, C-Therm Technologies, Canada), which is based upon a modified transient plane source method. This method is non-destructive and convenient. The TCi system consists of a sensor, power control device, and computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The heat that has been generated enters the material through the sensor during which a voltage decrease occurs rapidly at the heating source, and the thermal conductivity is calculated through the voltage decrease data. The testing capabilities of the system are 0–100 W/m K across a wide range of temperature (-50 to 200°C) and the accuracy of the instrument is better than 5%.

RESULTS AND DISCUSSION

Microstructures

Figure 1 shows representative SEM micrographs of the Al_2O_3 and GR, the size of the Al_2O_3 particles range from 7 μm to 0.8 μm [Figure 1(a)] and the averaged size was estimated about 1.4 μm from the high-resolution SEM image [Figure 1(b)]. A fluffy and crumpled morphology of GR can be observed from the Figure 1(c,d). GR varies from a few to several layers has wrinkles and folded regions with a lateral size of micrometers.

The typical XRD patterns of Al_2O_3, GR and composites were shown in Figure 2. The sharp peaks were observed at 25.58,
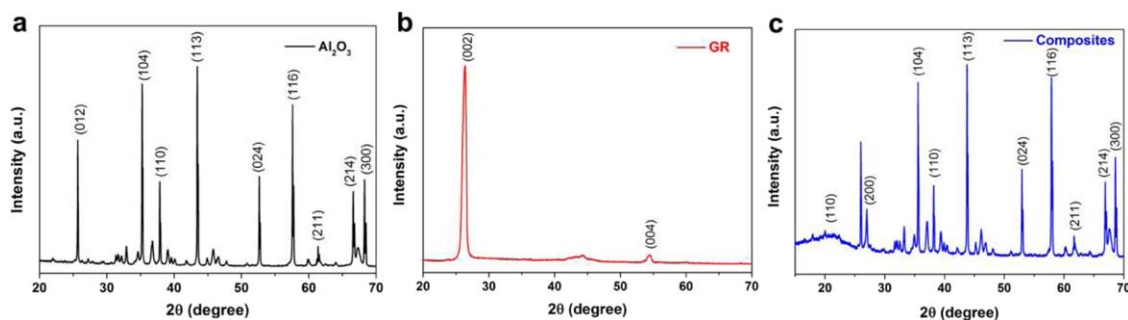
Figure 2. XRD patterns of Al_2O_3 particles (a), GR (b) and composites (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

35.15, 37.78, 43.36, 57.50°, respectively, indicating the high crystalline features of the Al_2O_3 phase. GR shows an intense peak around 24.38°, which may be attributed to the existence of $\pi-\pi$ stacking between the graphene sheets. Figure 2(c) depicts the XRD patterns of the as-prepared composites with Al_2O_3/GR weight ratios (64:1). Two different diffraction peaks were shown at 20.21 and 26.99°, respectively, correspond to the (110) and (020) crystallographic planes of an orthorhombic crystalline phase. The diffraction peaks around 26.01° was intense, which would suggest that the Al_2O_3 and GR are reassembled in the EVA.

Thermal Conductivity

Al_2O_3 has been widely used as the filler for thermal interface materials due to its relatively high thermal conductivity and insulating property. The content of fillers has a great effect on thermal conductivity of composite.[33] Figure 3(a) shows the thermal conductivity of EVA influenced by mass fraction of Al_2O_3 particles. It clearly shows that the thermal conductivity of EVA filled with fillers increases with the increase of mass fraction of Al_2O_3 particles. At low filler loading, the thermal conductivity increases slowly due to Al_2O_3 particles surrounded by matrix cannot touch each other and cause high thermal contact resistance inside the composites. With the Al_2O_3 addition percentage more than 30 wt %, the thermal impedance of the EVA becomes sharply increased. The maximum thermal conductivity is 2.26 ± 0.02 W/m K at the mass fraction of 80 wt % while the thermal conductivity of pure EVA is only 0.42 W/m K, which is

a 5-fold improvement and a little higher than that of thermal grease filled by Al_2O_3 in literatures.[29] The improved thermal conductivity could be attributed to the compact packing structure, which is favorable to decrease the thermal contact resistance at the high filler loading. However, further addition of Al_2O_3 in the experiment is adverse because of the hardening of the EVA. So higher thermally conductive fillers GR was suggested to further improve its thermal properties.

GR is known a promising filler to enhance thermal conductivity of polymer composites because of its high intrinsic thermal conductivity. Hence, GR was added into the EVA to enhance their heat conduction. The influences of GR and addition percentage on the thermal conductivity of EVA are shown in Figure 2(b). It can be found that GR is beneficial to improve their heat conduction. The thermal conductivity of the EVA was enhanced nearly linearly with the increasing GR and the thermal conductivity enhancement was nearly achieve to 80% in comparison to the unmodified one when the content of GR is 5 wt %. Considering the much higher specific surface of GR than Al_2O_3 particles, GR may induce the large viscosity increasing when further addition of GR.

Combination of several kinds of fillers has been testified to be a practical method to reduce the interfacial conduction resistance and improve the thermal conductivity of composites by some researchers.[28–30] In order to maximize the utilization of heat conduction offered by fillers, the GR and Al_2O_3 hybrid fillers are mixed with EVA to enhance their thermal conductivity. The
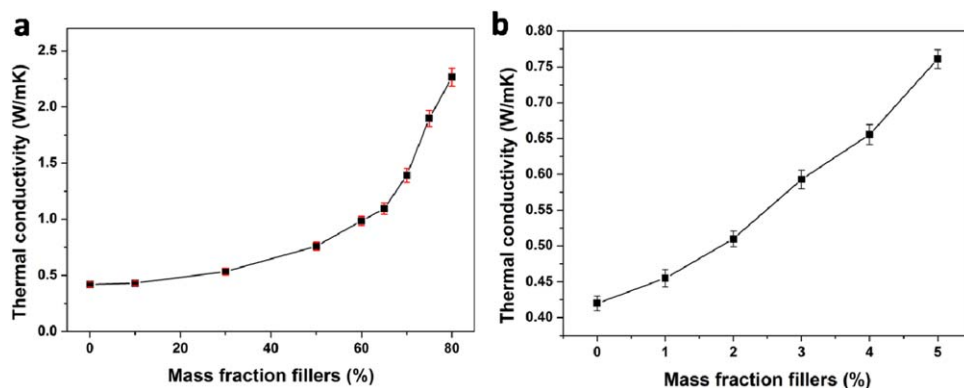

Figure 3. Thermal conductivity of EVA composite as a function of mass fraction of Al_2O_3 (a) and GR (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
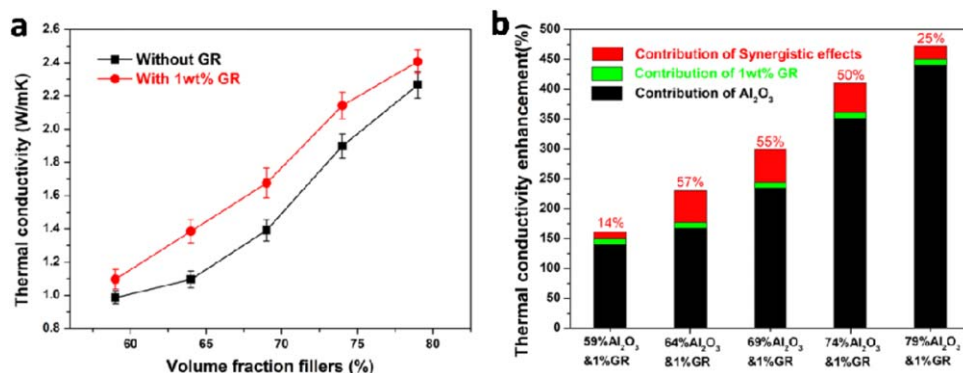
Figure 4. Comparison of thermal conductivity (a) and thermal conductivity enhancement (b) of EVA with and without GR at different filler loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal conductivity of composite presented in Figure 4 indicated a strong synergistic effect when GR is filled. With only Al_2O_3 (60–80 wt %) loading, the thermal conductivity is increased from 1.00 W/mK to 2.26 W/mK. It is worth noting that the thermal conductivity of the composite enhanced from 1.09 W/mK to 2.40 W/mK by addition of 1 wt % GR, and it reached as high as 2.40 ± 0.07 W/m K when the Al_2O_3 and GR content are 79 wt % and 1 wt %, which is higher than that without GR (2.26 ± 0.02 W/m K) and the only loading of 1 wt % GR. So a remarkable synergistic improvement on thermal conductivity of the novel EVA was observed. The strongest synergistic effect can be achieved around the loading of 64 wt % (Al_2O_3) and 1 wt % (GR), which could be attributed to the abundant thermal conductive networks offered by the mixed fillers. However, the synergistic effect slightly decreases by the further addition of Al_2O_3 due to the increased thermal conduction resistance associated with hetero-interfaces between fillers and matrix polymers. Although the enhancement is far weaker than our previous work, we believe that the thermal property can be greatly improved by optimization of the process and modification of Al_2O_3 and GR and then minimize the polymer/nanomaterial interfacial thermal resistance.[29]

To understand thermal transport in the composite, the three-dimensional schematic models of the synergistic effect were shown in Figure 5. From Figure 5(a), a compact structure of

heat conducting path can be easily formed by filling with Al_2O_3 particles, which is desired to minimize the scattering of phonons and enhance the thermal conductivity. However, it is still a lot of residual spaces that Al_2O_3 particles cannot occupy in EVA, which leads to a bad effect on further decrease the interfacial thermal contact resistance. Even though GR with superb thermal conductivity is crucial to enhance the thermal transfer, the poor dispersion and restacking of graphene sheets as well as the low content of GR in EVA is adverse to develop a heat conduction network [as shown in Figure 5(b)]. It was suggested by the results that the synergistic effect of the composites was obtained because the amount of thermally conductive fillers were increased by adding incorporated GR and three-dimensional thermal transfer pathway was formed between the Al_2O_3 and GR fillers owing to intrinsic structure of GR. The mechanism for improved thermal conductivity is as follows: GR can be effectively insert into the residual spaces and construct a strong three-dimensional networks as shown in Figure 5(c), this unique insertion effectively prevents the inter-sheet restacking of graphene sheets and build up a bridge between Al_2O_3 particles for thermal conductive pathways. The strong three dimensional heat transfer network is favorable to minimize the scattering of phonons and interfacial thermal contact resistance because of the enlarge contact area between thermally conductive fillers, and therefore enhance the thermal conductivity of the novel EVA.
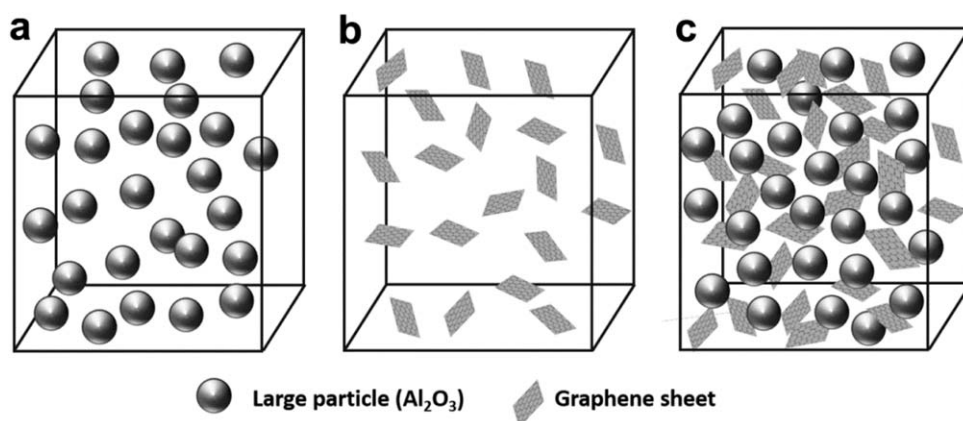

Figure 5. Schematics of the distribution of (a) Al_2O_3 particles, (b) GR and (c) hybrid filler of Al_2O_3/GR in EVA.

CONCLUSIONS

In summary, the present work has developed a novel approach to prepare EVA with improved thermal conductivity. Al_2O_3 particles, GR and Al_2O_3/GR were used as fillers, respectively. A strong synergistic effect was observed when filled Al_2O_3/GR into EVA, which could be attributed to the three-dimensional thermally conductive network constructed by hybrid fillers. This unique structure effectively prevents the inter-sheet restacking of graphene sheets and minimizes the thermal contact resistance between fillers and interface. The resultant exhibits a high thermal conductivity of 2.40 ± 0.07 W/m K which is much higher than single filler at the same loading. We also believe that the thermal property can be further improved by optimization of the content of hybrid fillers and processing and modification of Al_2O_3 and GR. With our approach it is possible to fabricate hybrid fillers based EVA with high thermal conductivity at low cost and environmentally friendly processing techniques, making it possible to be used in heat dissipation.

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